

Stanford Univ

(NASA CR 511003)

34 p.

UNPUBLISHED PRELIMINARY DATA

Membrane Separation

Jerry Lundstrom

Research Assistant, Department of Genetics.

① ~~School of medicine~~
Stanford University Medical School

~~Palo Alto, California~~

May, 1963

13 refs

(NASA Grant N5G-81-60)

N65 16326
 (ACCESSION NUMBER)
 34
 (PAGES)
 04
 (CATEGORY)
 04
 (CODE)
 04
 (THRU)
 04
 (CATEGORY)
 04
 (CODE)
 04
 (THRU)
 04
 (CATEGORY)

Available to non-USA and
 NASA only.

GPO PRICE \$ _____

OTS PRICE(S) \$ _____

Hard copy (HC) 2.00

Microfiche (MF) 50

Membrane Separation

1. Discussion of the permeability coefficient

As indicated in section 4.2 of the NASA report on contract NsG 81-60 covering the period of March 1962 to April 1963, the permeability coefficient can be obtained from either region (B) or (C) of the permeability curve (fig. 1). Most of the investigators working with gas-membrane-gas systems have preferred region (B) probably because it is more readily obtainable for systems of low permeability and also because by extrapolating the linear portion of the curve to the time axis, one can easily obtain the time-lag, L , and subsequently the diffusion coefficient, D , of the solute through the membrane by: (1)

$$1) \quad D = \frac{X^2}{6L} = \frac{X^2}{2T} \quad (2)$$

where

X = membrane thickness, cm

L = time-lag, sec

D = diffusion coefficient, cm^2/sec

T = time for steady-state, sec

~~Atmospheric~~
~~Pressure~~
~~Membrane~~
~~Separation~~
~~Process~~

The available experimental data for gas-membrane-gas systems has revealed that the permeability coefficient, K , can be described by the following relationship:⁽³⁾

$$2) \quad K = DS$$

where

$$K = \text{permeability coefficient, } \frac{\text{cm}^3 \text{ (STP) cm}}{\text{cm}^2 \text{ sec atm}}$$

$$S = \text{solubility of the solute in the membrane, } \frac{\text{cm}^3 \text{ (STP)}}{\text{cm}^3 \text{ atm}}$$

When the solute is a gas, then its solubility is proportional to the pressure in accordance with Henry's law, and its diffusion can be described by Fick's first law. The quantity of permeating gas, q , is then:⁽⁴⁾

$$3) \quad q = DSA \frac{(p_1 - p_2)}{x} t$$

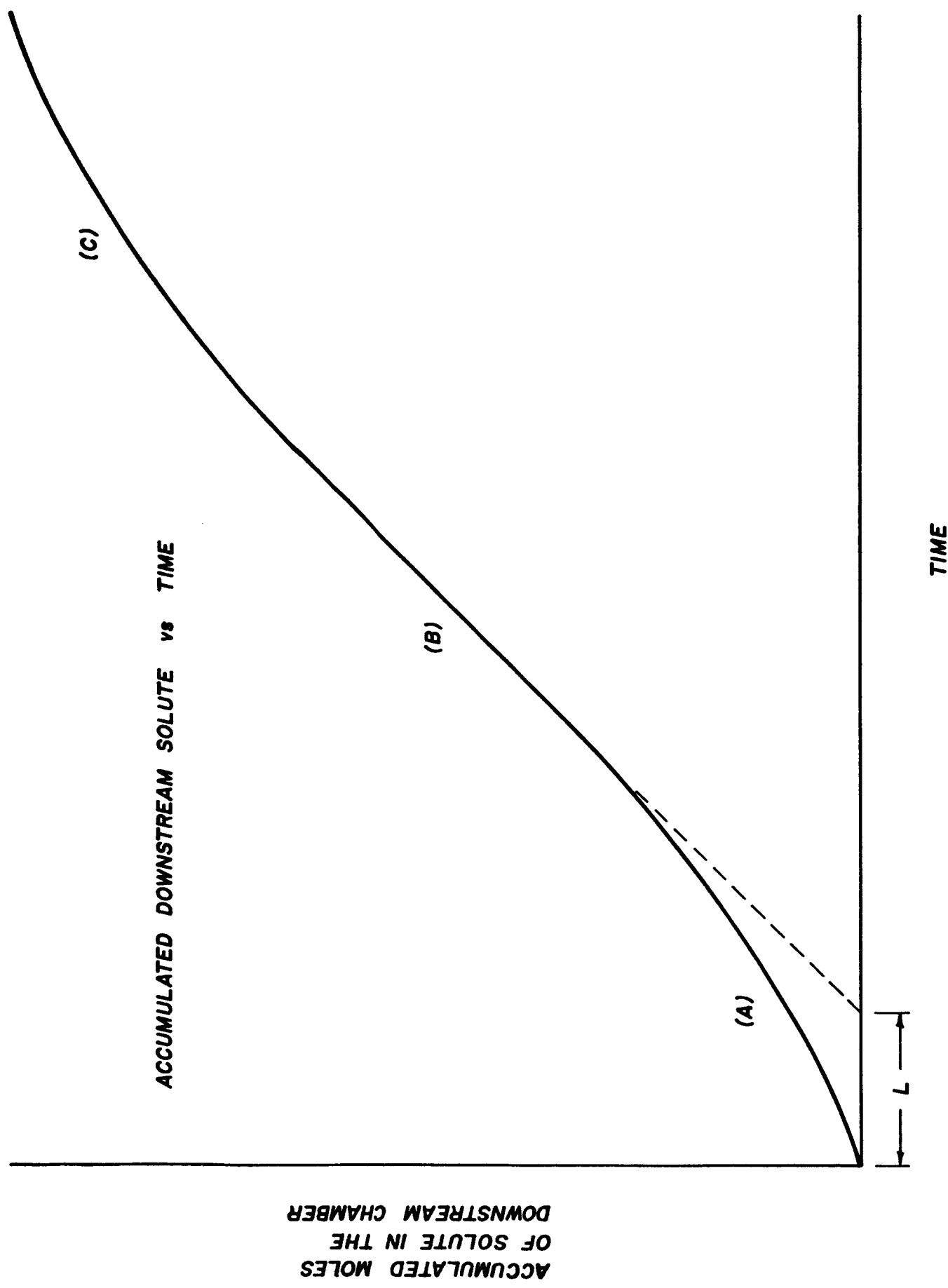
where

$$A = \text{membrane area, cm}^2$$

$$p_1 - p_2 = \text{pressure difference across the membrane, atm}$$

$$t = \text{time, sec}$$

$$q = \text{amount of gas, cm}^3 \text{ (STP)}$$



The units of S for a gas are the number of cm^3 of the gas at 0°C and 1 atmosphere pressure that dissolves in 1 cm^3 of the membrane per atmosphere pressure.⁽³⁾ The corresponding solubility of a solute dissolved in a solvent would be the number of mmoles of solute dissolving in 1 cm^3 of membrane at a given temperature per molar concentration of solute solution. In the solution case the pressure difference across the membrane is replaced by the concentration difference of the solute in mmoles of solute per ml of solution. The corresponding q is expressed as the number of mmoles of the solute.

At steady-state, q will be proportional to the pressure difference ($p_1 - p_2$) provided the pressures are not too great.⁽⁵⁾ As mentioned in section 4.2 of the NASA report, the permeability of CO_2 through rubber departs from this linear relationship. Diffusion of H_2 through rubber also exhibits a similar though less dramatic departure. Barrer⁽⁶⁾ suggests that this departure is not due to a breakdown of the perfect gas laws at these pressures, since Wustner's⁽⁷⁾ study of H_2 through silica with pressures up to 800 atmospheres showed linear permeation rate-pressure curves. One explanation of the enhanced permeability at high pressures is that the resulting high solubility of the gas tends to swell or deform the membrane by its high concentration and thereby decrease the activation energy barrier governing the diffusion rate. Systems in which the gas interacts with the membrane are numerous: typical of such systems are H_2O - nylon and H_2O - ethylcellulose. These systems have been studied by C. E. Rogers, et al.,⁽⁸⁾ with the conclusion that the departure from ideal behavior with increasing pressure is the result of swelling or plasticizing of

of the membrane by the H_2O vapor. That the enhanced permeability is related to some change in the diffusion process as opposed to a deviation from the solubility predicted by Henry's law is supported by the occurrence of the same phenomenon in a system that is independent of Henry's law, i.e., the diffusion in solid solutions of metals. Mantano⁽⁹⁾ has shown that the diffusion coefficient of copper in nickel is dependent on the concentration of copper in the nickel and that the diffusion coefficient increases rapidly when the copper concentration exceeds 70%.

Experimentally, K can be determined by plotting q versus t to obtain the slope in region (B) and then substituting the constant slope into the differential of q with respect to t (i.e., the differential of eq. 3):

$$4) \frac{dq}{dt} = DSA \frac{(p_1 - p_2)}{x} = KA \frac{(p_1 - p_2)}{x} = KA \frac{(c_1 - c_2)}{x}$$

where

$$C = \frac{p}{RT}, \text{ in } \frac{\text{mmoles}}{\text{ml}}$$

R = ideal gas constant

T = absolute temperature, °K

K in units of

$$\frac{\text{cm}^3 (\text{STP}) \text{ cm}}{\text{cm}^2 \text{ sec atm}} \text{ for the case of } (p_1 - p_2)$$

and

$$K \text{ in units of } \text{cm}^2/\text{sec} \text{ for the case of } (c_1 - c_2)$$

It can be seen that eq. 4 is of the same form as Fick's first law, i.e.,

$$J = -D \frac{dc}{dx}$$

where

$$J = \text{flow rate of solute, } \frac{\text{mmoles}}{\text{cm}^2 \text{ sec}}$$

$$D = \text{diffusion coefficient, cm}^2/\text{sec}$$

$$\frac{dc}{dx} = \text{concentration gradient, } \frac{\text{mmoles}}{\text{cm}}$$

so that when

$$J = \frac{dq}{dt} \frac{1}{A}$$

and

$$\frac{c_1 - c_2}{x} = \frac{-dc}{dx}$$

then

D in Fick's first law becomes the permeability coefficient, K.

Calculations of the permeability coefficient, K, in region (C) can be made by measuring the decrease in the upstream concentration with time. By assuming that the downstream concentration is negligible with respect to the upstream concentration, the depletion of the solute from the upstream chamber with time can be described as a first order process dependent only on the amount of solute in the upstream chamber, i.e.,

$$6) \quad -\frac{dn}{dt} = Hn$$

where

n = the mmoles of solute in the upstream chamber

H = a constant

$\frac{dn}{dt}$ = the change in the mmoles of solute in the upstream chamber with time.

rearranging and integrating

$$\int \frac{-dn}{n} = \int H dt$$

$$-\ln n = Ht + \text{constant}$$

evaluating the constant at

$$t = 0$$

$$-\ln n_0 = \text{constant}$$

so

$$-\ln n = Ht - \ln n_0$$

or

$$\ln n = -Ht + \ln n_0$$

$$7) \quad \underline{n = n_0 e^{-Ht}}$$

H can be evaluated by considering that:

$$\frac{-dn}{dt} = \frac{dq}{dt} \quad (\text{see eq. 4})$$

so that

$$\frac{dq}{dt} = Hn$$

where

$$\frac{dq}{dt} = \frac{KAC_1}{X}$$

and since

$$C_1 = \frac{n}{V_1}$$

where

$$V_1 = \text{upstream chamber volume, cm}^3$$

then

$$Hn = \frac{KA}{XV_1} n$$

or

$$H = \frac{KA}{XV_1}$$

and substituting this value into equation 7,

$$n = n_o e^{-\frac{KA}{XV_1} t}$$

Dividing both sides of the equation by V_1 , one obtains the upstream chamber solute concentration as a function of time:

$$8) \quad c_{1,t} = c_{1,o} e^{-\frac{KA}{XV_1} t}$$

Investigators using region (C) of the permeability curve (mainly those concerned with dialysis) have developed a somewhat independent set of units from the investigators using region (B) (mainly those concerned with

gas-membrane-gas systems). For example, Craig⁽¹⁰⁾ has chosen to record his data in units of half-escape times (the time need for $\frac{C_{1,t}}{C_{1,o}} = 1/2$). For fast

solute-membrane systems this is a convenient way to represent the data, provided the apparatus and membrane constants are given so that the half-escape times can be compared with other sources.

2. Values of the permeability coefficients for CO₂

In searching the literature for CO₂ permeability data, the following articles and books have been the most helpful and have provided CO₂ data for some 50 to 60 hydrophobic membranes:

1. R. M. Barrer, Diffusion in and Through Solids, Cambridge Univ. Press, N. Y. (1951)
2. D. W. Brubaker and K. Kammermeyer, IE/C 44 (1952) 1465
3. H. E. Huckins and K. Kammermeyer, Chem. Eng. Prog. 49 (1953) 180
4. K. Kammermeyer, IE/C 49 (1957) 1685
5. D. F. Othmer and G. J. Frohlich, IE/C 47 (1955) 1034
6. B. Ruedi et A. Fleisch, Helv. Physiol. Acta. 20 (1962) 193
7. S. B. Tuwiner, Diffusion and Membrane Technology, Reinhold Pub. Corp., N. Y. (1962)
8. G. J. van Amerongen, J. Appl. Physics 17 (1946) 972

In order to convert the permeability coefficients having a variety of units to the common units of cm^2/sec so that the coefficients could be easily compared and also in a form readily used in Fick's first law, the conversion factor of $8.31 \times 10 \frac{\text{cm}^3 \text{ cm Hg pressure difference}}{\text{cm}^3 (\text{STP})}$ was calculated for pressure differences measured at 25°C (sec. 5.5).

In the following table are listed the CO_2 permeability coefficients for some membranes that are highly permeable to CO_2 ; the coefficients have all been converted to units of cm^2/sec .

Table 1

Membranes of high CO_2 permeability

<u>Membrane</u>	<u>CO_2 permeability coefficient at room temperature</u>
Silicone rubber	$2 \text{ to } 3 \times 10^{-5}$ (4,6) (refs. listed above)
Polyvinyl chloride with 20 parts of di (2-ethyl hexyl) phthalate plasticizer	1×10^{-5} (2)
Natural rubber	1×10^{-6} (5,4)
Teflon	4×10^{-7} (6)
Polyethylene	1×10^{-7} (5,2)
Porous glass	5×10^{-4} (3)

The above coefficients are, in general, averages from more than one laboratory. Since the permeability coefficient is temperature dependent, i.e., $K = K_0 e^{-A/RT}$ where K_0 , A and R are constants, (3) and in some of the cases the temperatures

were somewhat different, these numbers represent approximations to the permeability at 25⁰ C. Although porous glass has the highest permeability coefficient to CO₂, it seems doubtful that it would be an effective barrier to glucose so that the most likely candidate for use in the separation of CO₂ from glucose is silicone rubber.

3. Preliminary results of the dye permeability studies

Of the hydrophobic membranes with high permeabilities to CO₂, silicone rubber, teflon and polyethylene have been measured for their permeability to Na₂FI (disodium fluorescein). The results are listed below.

Table 2

Apparent permeability coefficient at 25 ± 2⁰ C for Na₂FI

Membrane	Thickness	Upstream Concentration	K x 10 ¹⁴ , cm ² /sec			
			Time: 2 x 10 ⁵	1 x 10 ⁶	2 x 10 ⁶	4 x 10 ⁶ sec
Silicone rubber	7.7 mil	0.226 $\frac{\text{mmoles}}{\text{ml}}$	1.6	1.7	2.0	2.5
Teflon	0.5	0.101	6	4	3	2
Polyethylene	1.0	0.101	0.6	0.2	0.15	0.2

One curious result that has persisted in the polyethylene and teflon permeability studies is that the apparent permeability coefficient decreases with time and eventually reaches some minimum value. The proposed explanation of this apparent decrease in solute flow across the membrane is that due to the high concentrations

of dye used in the upstream chamber, there is a decrease in the effective concentration of free H_2O available in the upstream chamber since some of the H_2O is bound as hydrate complexes with the ionized dye. Probably the most stable hydrates are those formed with the sodium ions of the dye. The resulting free H_2O concentration difference across the membrane dictates a net back-diffusion of H_2O from the downstream chamber into the upstream chamber. This H_2O flow leaches some of the diffusing Na_2FI out of the membrane, returning it to the upstream chamber. Since the back-diffusion of H_2O increases with time to some steady-state flow, the apparent permeability of Na_2FI decreases with time to some minimum value. After the back-diffusion of H_2O has reached steady-state, the suspected result is that the apparent permeability coefficient of the Na_2FI will increase slowly since the time-lag for the Na_2FI is anticipated to be long compared to the time-lag for the back-diffusion of H_2O . The experiments to date provide inconclusive evidence for this latter point.

In some of the earlier experiments with polyethylene, less concentrated solutions and thicker membranes gave higher apparent permeability coefficients. Two results are tabulated below (the two values are independent experiments).

Table 3
 Na_2FI - Polyethylene Apparent
 Permeability Coefficients at $25 \pm 2^\circ C$

<u>Upstream Concentration</u>	<u>Thickness</u>	<u>Time: 3.43×10^5 sec</u>	<u>4.11×10^5 sec</u>
$0.023 \frac{\text{mmoles}}{\text{ml}}$	2 mil	$3 \times 10^{-14} \text{ cm}^2/\text{sec}$	$2 \times 10^{-14} \text{ cm}^2/\text{sec}$

These results are consistent with the resisted permeability hypothesis since the back-diffusion of H_2O would be decreased by the increased membrane thickness and by the decreased upstream concentration, thereby increasing the apparent permeability coefficient. It seems probable that the increased thickness argument is applicable in explaining why the apparent permeability coefficient does not decrease with time in the case of the silicone rubber but does decrease with the thinner membranes of teflon and polyethylene (table 2). Some experiments using thicker sheets of polyethylene and teflon could prove to be enlightening on this point.

Potter, et al.,⁽¹¹⁾ have studied the effect of H_2O vapor on the permeability of O_2 through polyvinyl chloride and nylon. Their data showed that the apparent permeability of O_2 is assisted by H_2O vapor diffusing in the same direction and is resisted by H_2O vapor diffusing in the opposite direction.

An experiment now in progress to investigate the hypothesis of resisted permeability indicates that Na_2F diffusion through teflon is resisted by a factor of about 30, if the upstream solvent is ethanol and if the downstream solvent is H_2O over the reverse situation. This data is tabulated in table 4. A technical report by DuPont for the permeability of teflon to vapors gives the permeability of H_2O vapor as 10^3 times the permeability of ethanol vapor.⁽¹²⁾

Table 4

Na₂Fl - teflon apparent permeability coefficients at $25 \pm 2^\circ \text{C}$

Na₂Fl concentration = $2.2 \text{ to } 2.3 \times 10^{-1} \frac{\text{mmoles}}{\text{ml}}$

<u>Upstream Solvent</u>	<u>Downstream Solvent</u>	$K, \text{ cm}^2/\text{sec}$ $t = 1.6 \times 10^5 \text{ sec}$
H ₂ O	Ethanol	6×10^{-14}
Ethanol	H ₂ O	2×10^{-15}

The apparent permeability coefficients given in tables 2,3 and 4 are the integral coefficients, i.e., they have been calculated from the total amount of Na₂Fl diffusing through the membrane during the total time of the run, whereas the coefficients usually are expressed as a differential coefficient and are found from the slope of the permeability curve at some time, e.g., in region (B) of the permeability curve. The integral permeability coefficients for the Na₂Fl-hydrophobic membrane case (and in general for the substrate-hydrophobic membrane case) are the most useful since they are easily converted to the total amount of solute leakage occurring during a given period of time (the period starting with time = 0).

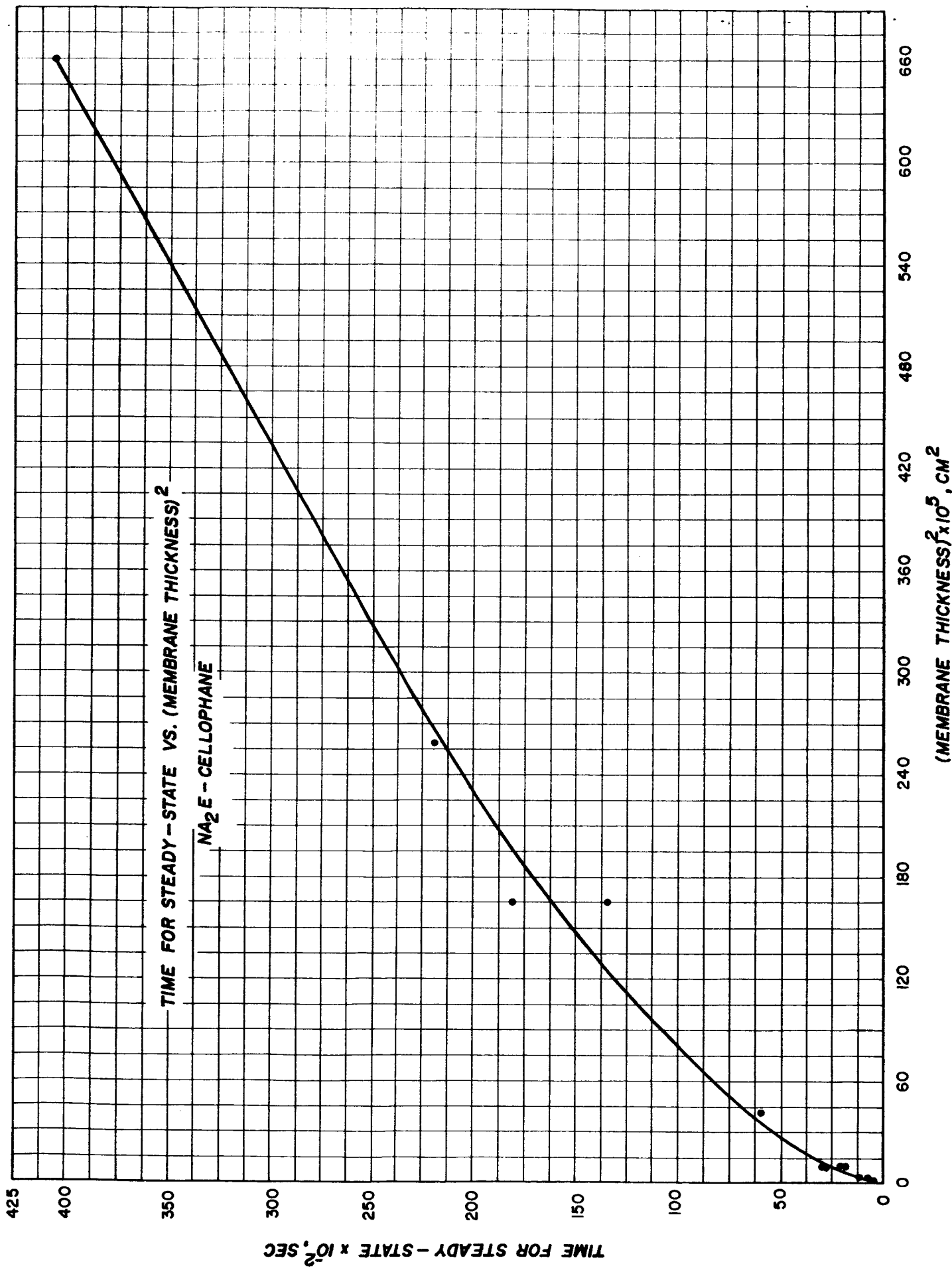
It was found for Na₂Fl and Na₂E (disodium eosin) permeability to cellophane that for a given concentration, the time for steady-state increased as the membrane thickness increased (table 5). Plots of time for steady-state versus the square of the membrane thickness for a constant upstream concentration of

Table 5

Na₂E - Cellophane permeability at 25 ± 2°C

<u>Upstream Concentration</u>	<u>Membrane^a Thickness</u>	<u>(Membrane)² (Thickness)</u>	<u>Time for Steady-State, sec</u>
$1.61 \times 10^{-1} \frac{\text{mmoles}}{\text{ml}}$	1.5 mil	$1.4 \times 10^{-5} \text{ cm}^2$	$7.2 \times 10^2 \text{ sec}$
1.61×10^{-1}	1.5	1.4×10^{-5}	5.4×10^2
1.61×10^{-1}	1.5	1.4×10^{-5}	5.7×10^2
1.61×10^{-1}	1.75	2.0×10^{-5}	7.2×10^2
1.61×10^{-1}	4.0	1.0×10^{-4}	2.2×10^3
1.61×10^{-1}	4.0	1.0×10^{-4}	2.9×10^3
1.56×10^{-1}	4.0	1.0×10^{-4}	2.7×10^3
1.56×10^{-1}	4.0	1.0×10^{-4}	1.8×10^3
1.56×10^{-1}	8.0	4.1×10^{-4}	5.9×10^3
1.56×10^{-1}	16.0	1.6×10^{-3}	1.8×10^4
1.62×10^{-1}	16.0	1.6×10^{-3}	1.3×10^4
1.62×10^{-1}	20.0	2.6×10^{-3}	2.2×10^4
1.61×10^{-1}	32.0	6.6×10^{-3}	4.1×10^4

^a All thickness measurements are for dry membranes.



dye have a decreasing slope with increasing membrane thickness (fig. 2). The rate of decrease of the slope also decreases with increasing membrane thickness. Since the diffusion coefficient is equal to the reciprocal of twice the slope (equation 1), the diffusion coefficient is increasing with increasing membrane thickness to some constant value suggesting the effect of resisted permeability by H_2O decreases with membrane thickness. In the absence of the back-diffusion of H_2O this data suggests the relationship of time for steady-state and membrane thickness agrees with that found in the case of gas-membrane-gas systems, i.e.,

$$T = B X^2$$

where

T = time for steady-state, sec

B = a constant

X = membrane thickness, cm

The experiments where the membrane thickness is held constant and the upstream concentration is varied are complicated by the additional factor that the membrane is swelled or distorted by the solute. The expected decrease in permeability of the solute when the upstream concentration is increased due to enhanced back-diffusion of H_2O is overcome by the augmented permeability due to increased swelling of the membrane by the solute. Interplay between the two factors is intensified at high concentrations so that the measurements of the time for steady-state dependence on membrane thickness for a high upstream concentration are meaningful over only a limited thickness range, and likewise the measurements of the time for steady-state dependence on upstream concentration

for a constant membrane thickness are meaningful only over a limited concentration range where the effect of back-diffusion of H_2O is somewhat constant if not negligible.

Using 4.0 mil thick cellophane that has been soaked in H_2O for longer than one day prior to the experiment and various concentrations of Na_2E , the corresponding time for steady-state and the apparent permeability coefficients have been measured. The results are given in table 6.

The 4.0 mil thick cellophane has given the most consistent results for the effect of concentration on the time for steady-state experiments (compared to the other single sheet thicknesses of 1.5 and 1.75 mil), however, at the high concentrations this system also suffers from the effects of the swelling-back diffusion interaction in addition to the complications of fluorescence measurements that accompanies the measurements of high concentrations.

When the log of the time for steady-state is plotted versus the reciprocal of the concentration, the curve becomes linear in the region of low concentration, and the corresponding plot of the time for steady-state becomes linear in the region of high concentration (fig. 3). These results indicate that the time for steady-state, T , is proportional to both the reciprocal of the concentration and the exponential of the reciprocal of the concentration. These relationships can take two possible forms:

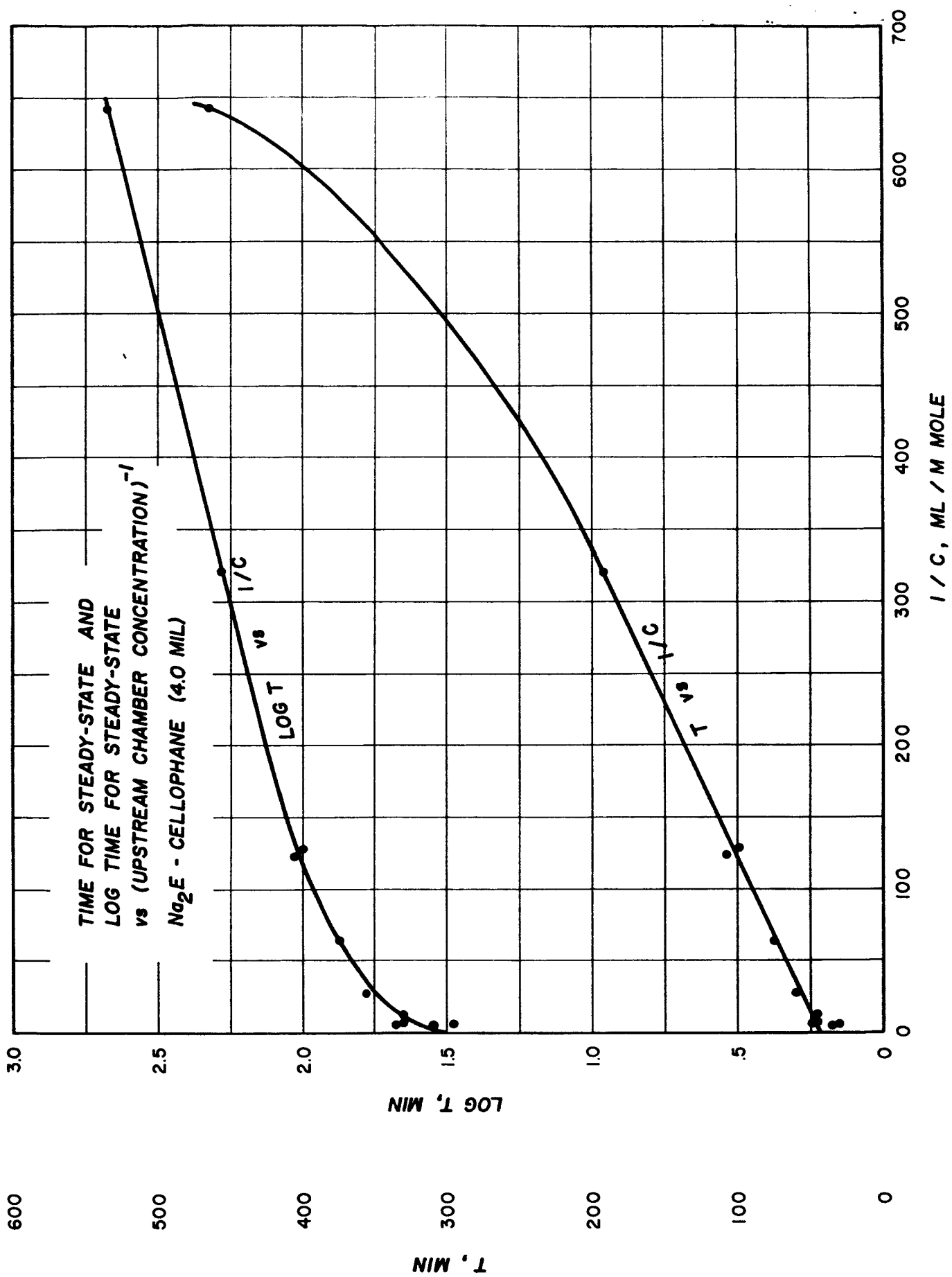


Table 6

Na₂E - Cellophane (4.0 mil) permeability at $25 \pm 2^\circ \text{C}$

<u>Upstream Concentration</u>	<u>Time for Steady-State</u>	<u>K</u>	<u>$D = \frac{X^2}{2T}$</u>
$1.61 \times 10^{-1} \frac{\text{mmoles}}{\text{ml}}$	48 min	$3.4 \times 10^{-8} \text{ a cm}^2/\text{sec}$	$1.8 \times 10^{-8} \text{ cm}^2/\text{sec}$
1.61×10^{-1}	36	2.8×10^{-8}	2.4×10^{-8}
1.56×10^{-1}	45	2.6×10^{-8}	1.9×10^{-8}
1.56×10^{-1}	30	3.5×10^{-8}	2.8×10^{-8}
7.80×10^{-2}	45	3.2×10^{-8}	1.9×10^{-8}
3.12×10^{-2}	60	3.7×10^{-8}	1.4×10^{-8}
1.56×10^{-2}	75	$2.5 \times 10^{-8} \text{ a}$	1.1×10^{-8}
8.07×10^{-3}	108	$2.25 \times 10^{-8} \text{ a}$	7.9×10^{-9}
7.80×10^{-3}	99	$2.32 \times 10^{-8} \text{ a}$	8.6×10^{-9}
3.12×10^{-3}	192	$1.58 \times 10^{-8} \text{ a}$	4.5×10^{-9}
1.56×10^{-3}	465	$1.26 \times 10^{-8} \text{ a}$	1.8×10^{-9}

a = indicates the more accurate data with respect to the fluorescence measurements.

$$T \propto \frac{1}{C} e^{1/C}$$

or

$$T \propto \frac{1}{C} + e^{1/C}$$

Since the diffusion coefficient, D , is proportional to the reciprocal of T (eq. 1) then,

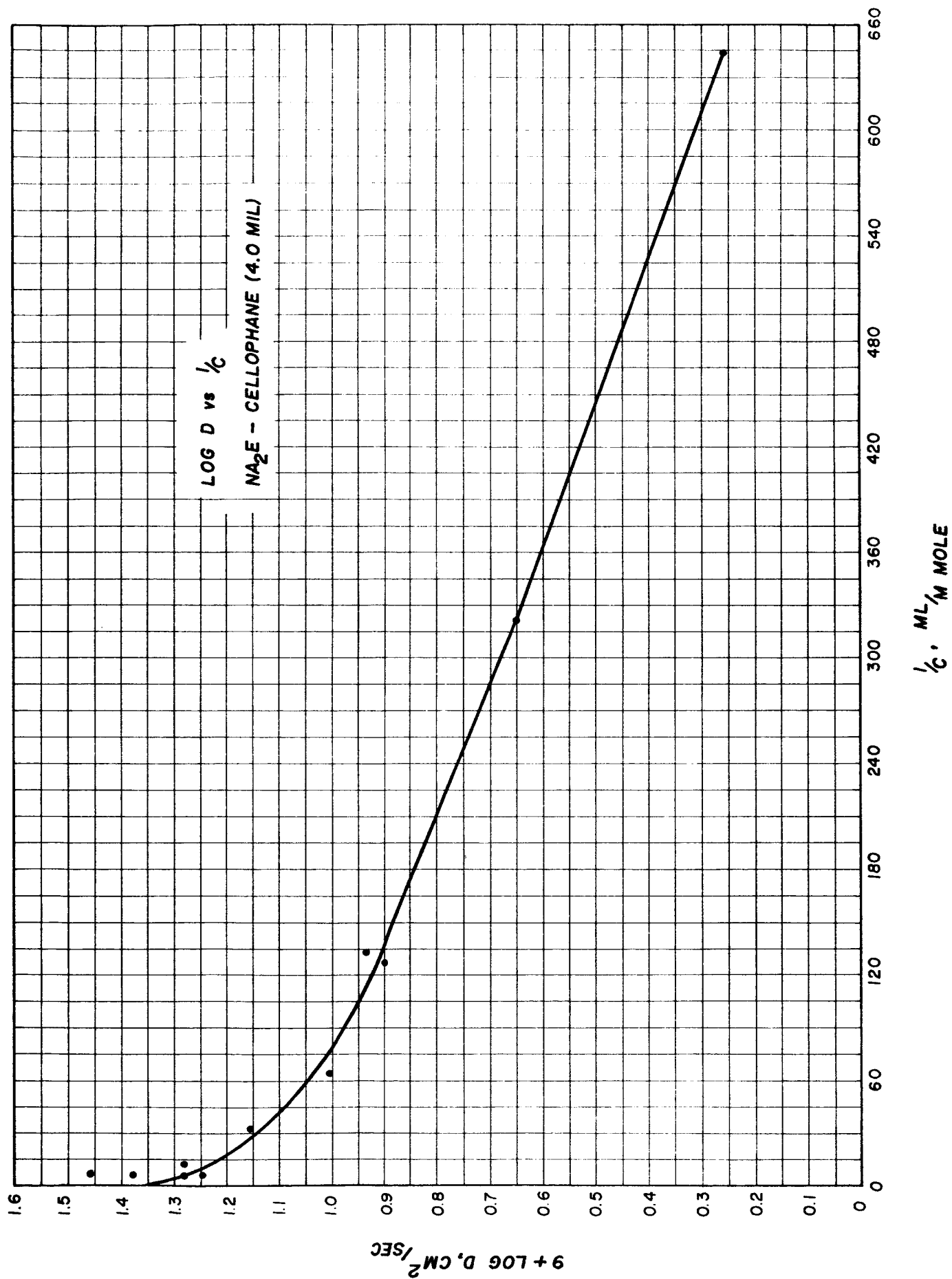
$$D \propto C e^{-1/C}$$

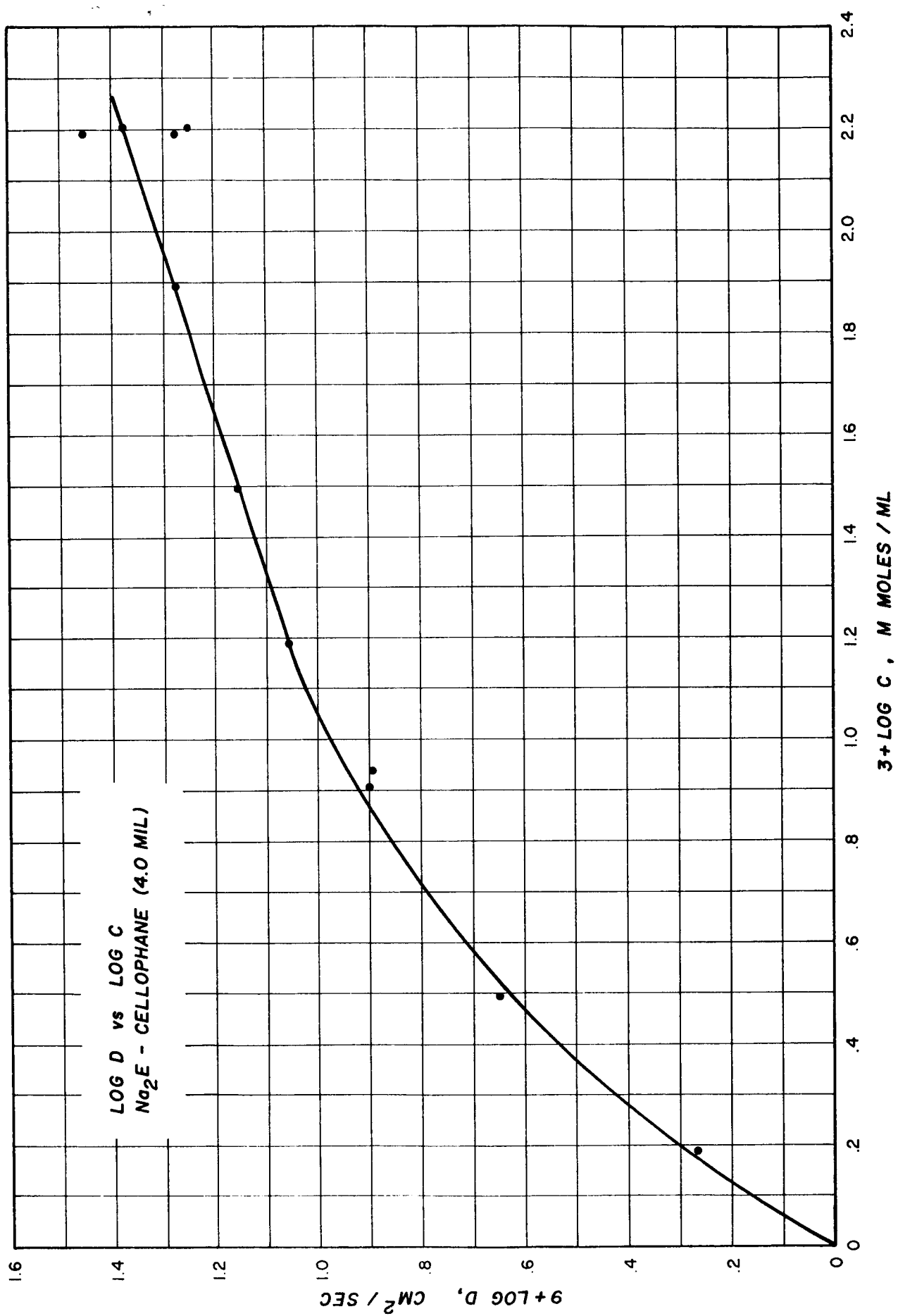
or

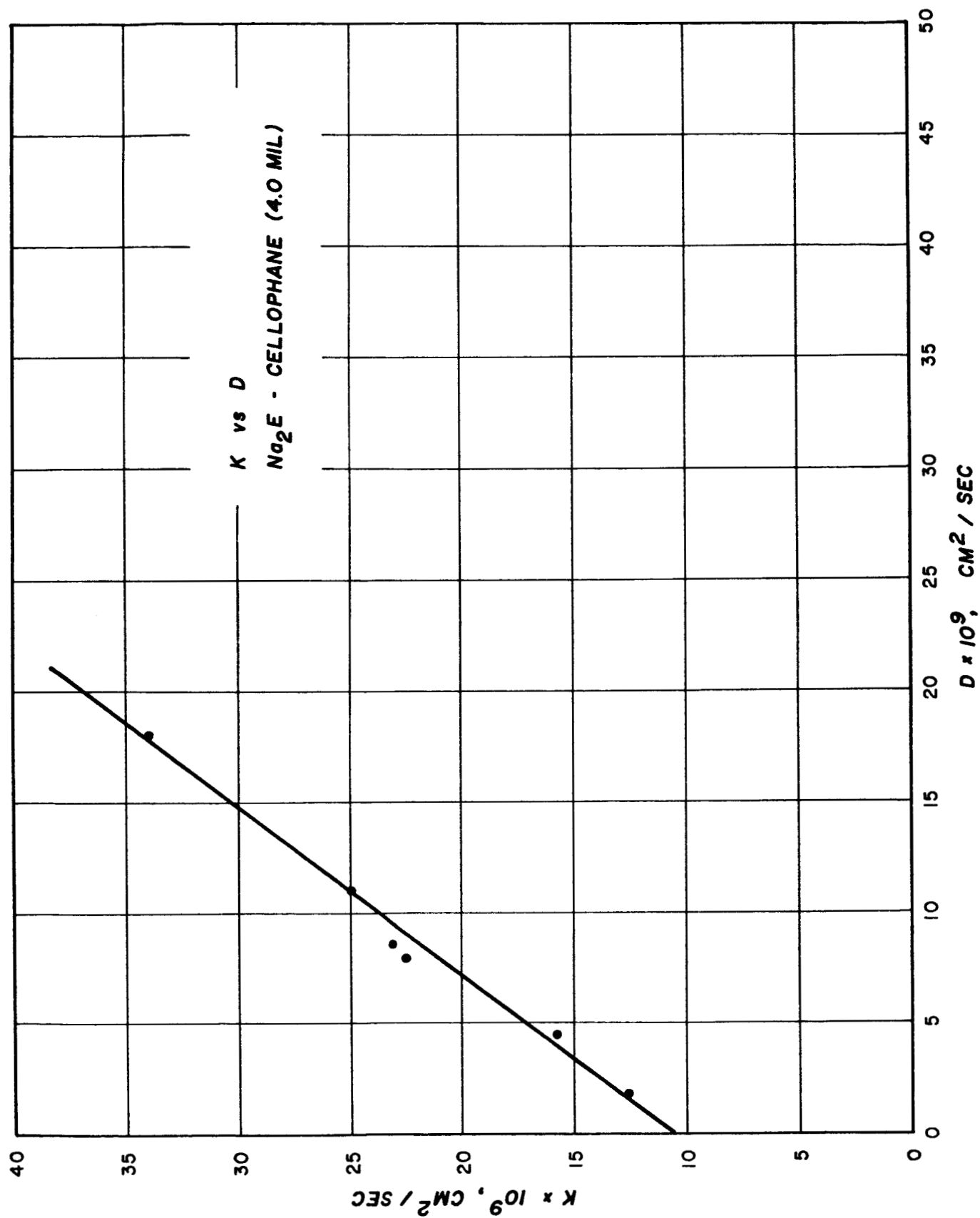
$$D \propto \frac{1}{1/C + e^{1/C}}$$

The plot of $\log D$ versus $1/C$ appears to be linear at large $1/C$ and the plot of $\log D$ versus $\log C$ appears to be linear at large $\log C$, however, the slope of the $\log D$ versus $\log C$ plot is disturbingly $1/3$ instead of the expected 1 from the above equations (figs. 4,5). The plot of the best K values (classified in terms of the estimated error of the fluorescence measurements) versus the D values is linear with a slope of 1.4 (fig. 6). This corresponds to the solubility of Na_2E in cellophane expressed in units of $\text{mmoles of Na}_2\text{E per cm}^3$ of cellophane per molar solution of Na_2E in H_2O (eq. 2).

All of the permeability data for the dye-cellophane experiments were obtained using flow permeability cells. The flow cell differs from the typical no-flow cell in that the downstream chamber of the flow cell is swept out by a constant flow of H_2O in order that the concentration in the downstream chamber be maintained negligible with respect to the upstream







concentration. The flow cells are useful for studying fast membrane-solute systems, since one can still obtain the two important measurements of time for steady-state and the value of the steady-state solute flow through the membrane.

Several experiments with the dye-cellophane system now appear to be important before any definitive statements about the general solute-cellophane system can be made. First, more data using thicker membranes than 4.0 mil that verify the above relationships are needed. Second, the permeability and time for steady-state of dyes having different molecular weights from Na_2E and Na_2FI should be measured to investigate the relationship between the time for steady-state and the permeability coefficient. Third, the effect of pH on the permeability of at least one dye should be investigated for comparison of the permeability of the possible ionic and molecular species of the dye. Finally, an experiment using solutions of constant NaCl concentration in attempts to minimize the back-diffusion of H_2O should be conducted. One obvious difficulty with this latter experiment is that the presence of NaCl may overpower the effect of the dye concentration on the permeability of the dye.

4. Discussion of the separation of CO_2 from glucose

Using the permeability data for Na_2FI through silicone rubber as a crude approximation to the permeability of organic metabolites and the published

data for CO_2 permeability, one can approximate the separation that a silicone rubber membrane would provide in a life-detection device. For a 1 cm^3 reaction chamber with a membrane area of 1 cm^2 , the thickness of the membrane needed can be estimated from equation 4, if the concentration of glucose in the reaction chamber is 10^{-3} molar and the amount of glucose diffusing through the membrane during the first 20 hours of the experiment is required to be no more than:

$$q_{\text{glucose}} = 7 \times 10^{10} \text{ molecules (sec. 5.4)}$$

$$K_{\text{glucose}} \approx K_{\text{Na}_2\text{FI}} = 1.6 \times 10^{-14} \text{ cm}^2/\text{sec at } t = 2 \times 10^5 \text{ sec (table 2)}$$

$$t = 20 \text{ hours} = 7.2 \times 10^4 \text{ seconds}$$

$$C_1 = 10^{-3} \frac{\text{mmoles}}{\text{ml}}$$

$$A = 1.0 \text{ cm}^2$$

$$X = \frac{KAC_1 t}{q} \quad (\text{eq. 4})$$

$$X = \frac{(1.6 \times 10^{-14}) (1.0) (10^{-3}) (7.2 \times 10^4)}{(10^{-10})}$$

$$X = 1.2 \times 10^{-2} \text{ cm}$$

For the same membrane and reaction chamber dimensions, the time needed to deplete 90% of the CO_2 produced in the first 16 hours from the reaction (the amount of CO_2 corresponding to the detectability limit of 10^2 dpm) assuming the time for steady-state is negligible, can be calculated using equation 8:

$$C_{1,t} = 10\% C_{1,o}$$

so

$$C_{1,t} = C_{1,o} e^{\frac{-KAt}{XV_1}} \quad (\text{eq. 8})$$

$$\text{becomes} \quad 10^{-1} = e^{\frac{-(3 \times 10^{-5}) (1.0)}{(1.2 \times 10^{-2}) (1.0)} t}$$

$$\ln 10^{-1} = -2.5 \times 10^{-3} t$$

$$-2.3 = -2.5 \times 10^{-3} t$$

$$t = 9.2 \times 10^2 \text{ sec} = 15 \text{ min}$$

where

$$K_{CO_2} = 3 \times 10^{-5} \text{ cm}^2/\text{sec} \quad (\text{table 1})$$

$$V_1 = 1.0 \text{ cm}^3$$

$$A = 1.0 \text{ cm}^2$$

$$X = 1.2 \times 10^{-2} \text{ cm}$$

We have not found data for the diffusion coefficient of CO_2 through silicone rubber so that the assumption that the time for steady-state is negligible can not be checked directly. A rough approximation, however, might be gained by substituting K into equation 1 for D . Some justification for this is offered by data reported by van Amerongen for the permeability of CO_2 through various types of rubber, all of which had $D \geq K$. (3)

The time for steady-state then is approximately,

$$T = \frac{(1.2 \times 10^{-2})^2}{(2) (3 \times 10^{-5})} = 2.4 \text{ sec}$$

Thus, we would predict that a 1 cm scale device, with a silicone rubber membrane .012 cm thick would exclude Na_2FI (? also glucose) to a level beneath the ultimate detectivity of C^{14} , and transmit 90% of the labelled CO_2 produced within the very reasonable interval of 15 minutes. As mentioned in section 4.2 of the NASA report, further studies on labelled metabolites will soon be under way.

5. Calculations

5.1 Theoretical maximum specific activity for carbon-14:

$$\frac{dn}{dt} = N_0$$

where

$$= \frac{.693}{t_{1/2}}$$

$$t_{1/2}(\text{half-life}) = 5.60 \times 10^3 \text{ years} = 2.94 \times 10^9 \text{ min}$$

if

$$N_0 = 1 \text{ mg-atom}$$

then

$$\frac{dn}{dt} = \frac{(.693) (6.023 \times 10^{20} \text{ disintegrations/mg-atom})}{2.94 \times 10^9 \text{ min}}$$

$$\frac{dn}{dt} = 1.42 \times 10^{11} \text{ dpm/mg-atom}$$

$$1 \text{ mcurie} = 2.2 \times 10^9 \text{ dpm}$$

so

$$\text{maximum specific activity} = \frac{1.42 \times 10^{11} \text{ dpm/mg-atom}}{2.2 \times 10^9 \text{ dpm/mc}}$$

$$\text{Maximum specific activity} = 65 \text{ mc/mg-atom}$$

5.2 Minimum number of molecules of CO_2 detectable:

$$\text{number of molecules} = \frac{(10^2 \text{ dpm}) (6 \times 10^{20} \text{ molecules/mmole})}{(65 \frac{\text{mc}}{\text{mmole}}) (2.2 \times 10^9 \frac{\text{dpm}}{\text{mc}})} = 4.2 \times 10^{11} \text{ molecules}$$

5.3 Time needed for an E. Coli to produce 4.7×10^{11} molecules of CO_2 :

The data are given by Clifton.⁽¹⁴⁾

Rate of CO_2 production

<u>Time, hour</u>	<u>$\text{mm}^3 \times 10^{-8}/\text{cell}/\text{hour}$</u>	<u>molecules $\times 10^9/\text{cell}/\text{hour}$</u>
0	---	---
1	3.8	1.0
2	6.7	1.8
3	10.4	2.8
4	11.1	3.0
5	14.7	4.0
6	7.8	2.1

conversion factor for mm^3 to molecules: Assuming that the volume of CO_2 is measured at STP

then

$$\text{number of molecules} = (6 \times 10^{23} \frac{\text{molecules}}{\text{mole}}) \frac{(1.0 \text{ mm}^3) (10^{-6} \text{ l/mm}^3)}{22.4 \text{ l/mole}} = 2.7 \times 10^{16} \text{ molecules}$$

so

$$1 \text{ mm}^3/\text{cell}/\text{hour} = 2.7 \times 10^{16} \text{ molecules/cell}/\text{hour}$$

The average CO_2 production rate over the six-hour period = 2.4×10^9 molecules/cell/hour

so

the time needed to produce 4.7×10^{11} molecules of CO_2 /bacterium is:

$$\text{time} = \frac{4.7 \times 10^{11}}{2.4 \times 10^9} = 2 \times 10^2 \text{ hours}$$

5.4 Upper limit to amount of glucose that is allowed to diffuse into the detection chamber during the first 20 hours of the experiment.

$$\text{specific activity of glucose} = \frac{(6 \text{ mg-atoms of C})}{(\text{mmole of glucose})} \frac{(65 \text{ mc})}{(\text{mg-atom of C})} = \frac{390 \text{ mc}}{\text{mmole of glucose}}$$

$$\text{molecules of glucose} = \frac{(10^2 \text{ dpm})}{(3.90 \times 10^2 \frac{\text{mc}}{\text{mmole}})} \frac{(6 \times 10^{20} \text{ molecules/mmole})}{(2.2 \times 10^9 \frac{\text{dpm}}{\text{mc}})} = 7 \times 10^{10} \text{ molecules}$$

5.5 Calculation of the conversion factor for pressure difference to

$$\text{concentration difference, i.e., units of } \frac{\text{cm}^3 (\text{STP}) \text{ cm}}{\text{cm}^2 \text{ sec cm Hg}} \text{ to } \frac{\text{cm mole}}{\text{cm}^2 \text{ sec } \frac{\text{mole}}{\text{cm}^3}}$$

or

$$\text{cm}^2/\text{sec}$$

$$1 \text{ cm}^3 (\text{STP}) = \frac{10^{-3} \text{ moles}}{22.4} = 4.46 \times 10^{-5} \text{ moles}$$

$$(C_1 - C_2) = \frac{10^{-3}}{RT} (P_1 - P_2)$$

where

p_1 and p_2 are in atmospheres.

Since the pressures are usually measured at 25°C ,

let

$$p_1 - p_2 = 1 \text{ cm Hg at } 25^\circ \text{C}$$

then

$$\frac{\Delta c}{\text{cm Hg}} = \frac{(10^{-3} \text{ l/cm}^3) (1 \text{ atm}/76 \text{ cm/Hg})}{(.082 \frac{\text{l-atm}}{\text{mole}^\circ \text{K}}) (298^\circ \text{K})} = 5.38 \times 10^{-7} \frac{\text{moles}}{\text{cm}^3 \text{ cm Hg}}$$

$$\text{The conversion factor} = \frac{4.46 \times 10^{-5} \frac{\text{moles}}{\text{cm}^3 (\text{STP})}}{5.38 \times 10^{-7} \frac{\text{moles}}{\text{cm}^3 \text{ cm Hg}}} = 8.31 \times 10 \frac{\text{cm}^3 \text{ cm Hg}}{\text{cm}^3 (\text{STP})}$$

References

1. H.A. Daynes, Proc. Roy. Soc. A97 (1920) pp. 286
2. G.J. van Amerongen, Rubber Chem. & Technol. 28 (1955) pp. 821
3. G.J. van Amerongen, J. Appl. Physics 17 (1946) pp. 972
4. S. von Wroblewski, Ann. Physik. Chemie 8 (1879) pp. 29
5. J. Dewar, Proc. Roy. Instn. 21 (1914) pp. 813
6. R.M. Barrer, Diffusion in and Through Solids, Cambridge Univ. Press, N.Y. (1951) pp. 404
7. H. Wustner, Ann. Phys. Lpz. 46 (1915) pp. 1095
8. C.E. Rogers, et al., IE/C 49 (1957) pp. 1933
9. C. Mantano, Japanese J. Phys. 8 (1933) pp. 109
10. L.C. Craig and A.O. Pulley, Biochem. 1 (1962) pp. 89
11. E.C. Potter, et al., J. Appl. Chem. 10 (1960) pp. 48
12. Permeability of Gases and Vapors Through DuPont Industrial Films, Film Dept., E.I. Dupont DeNemours & Co., Los Angeles 58, Calif.
13. C.E. Clifton, Introduction to Bacterial Physiology, McGraw-Hill, N.Y. (1957) pp. 305